INSTITUTE NOTES.

JANUARY 1941.

FORTHCOMING MEETINGS.

Wednesday, February 5th, at 2.15 p.m. "Addition Agents for Lubricating Oils," by E. A. Evans, M.I.A.E., F.C.S. (Chairman, Lubricating Oil Group).

This meeting will be held at the Institution of Mechanical Engineers, Storey's Gate, London, S.W.1.

CONSISTENCY OF GREASE.

The Grease Panel of the Institute (Chairman Mr. E. A. Evans) has for some time been considering the whole question of the standardization of methods of testing greases. Members and companies are invited to send to the Assistant Secretary a description of their own procedure for the determination of the *consistency of grease*. It is hoped to have available for consideration by the Panel a complete survey of the methods employed for this determination. Any comments on the methods or results of experience will be of considerable value to the Panel in their discussions and will be welcomed.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Fellow, Member, or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

CROOK, Roy Dallas, B.Sc., Chemist, Shell Company of Australia, Adelaide, S. Australia. (*T. Hartigan ; H. A. Banks.*)

FORD, Alexander Langridge, B.Sc., Chemist, Anglo-American Oil Co., Ltd. (*C. Chilvers ; E. B. Evans.*)

MACKIE, William Frederick Charles, Shell Marketing & Refining Co. (*G. Davidson ; E. LeQ. Herbert.*) (*Trans. to Fellow.*)

OOSTEN, William Hennanus (Dutch), General Manager, Bataafsche Petroleum Mij., Middlesex. (*J. Kewley ; J. H. Blakiston.*)

PENARD, Herbert F. L. (Dutch), Consulting Engineer, 53 Clifford's Inn, London, W.C.2. (*G. H. Cozon ; C. E. Spearing.*)

WITHERS, George, Lubrication Engineer, Texas Co. (S.A.), Ltd., Johannesburg. (*W. E. Gooday ; E. W. Ramsay.*)

Applications for admission as Students.

DRIVER, Antony Victor, Shell Marketing & Refining Co's Laboratory. (*H. E. Priston ; R. G. Strickland.*)

KEEN, Sidney, Student, Royal School of Mines. (*S. E. Coomber ; G. D. Hobson.*)

POOLE, Walter George, Student, Royal School of Mines. (*S. E. Coomber ; G. D. Hobson.*)

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STUDIES ON THE SEPARATION OF PARAFFIN WAXES. PART III.—THE SWEATING OF OIL-FREE WAXES.*

By M. F. Sawyer, Ph.D., A.M.Inst. Pet., T. G. Hunter, D.Sc., F.Inst.Pet., and A. W. Nash, M.Sc., F.Inst.Pet.

The production of paraffin wax from wax distillate may be considered to take place in the following stages :—

(1) Partial removal of the oil by chilling and filter pressing ;
(2) Removal of oil and waxes of low melting point from the wax cake by the process of fractional melting—the so-called sweating process ; and
(3) Physical or chemical refining of the sweated wax.

It has previously been stated[1] that this research project is concerned primarily with the sweating stage, the principle of this operation being based on the fact that the various waxes comprising the slack wax have progressively higher melting points. The fractions removed contain valuable products, and re-sweating is therefore an important feature of the commercial process. Innumerable combinations of re-sweating are possible to give a wide range of products differing in melting point and oil content, but the investigation of this is outside the scope of the present paper, which is concerned with the fractional melting of oil-free waxes.

The efficiency of the sweating or fractional melting operation is dependent on some or all of the following factors :—

(1) The sweating equipment.
(2) The rate of sweating.
(3) The size and shape of the wax crystals, which may be affected by—
  (*a*) Composition of the wax.
  (*b*) Amount of oil present in the oil–wax mixture comprising the slack wax.
  (*c*) Viscosity of the oil; and
  (*d*) Treatment of the wax–oil mixture prior to sweating (*e.g.*, the crystal size may be affected by the rate of cooling in the sweater).

It should be noted, however, that there is no general agreement that all the above factors contribute towards the efficiency of the process. It is clear that if a single wax stock and the same sweater are employed throughout the investigation, the effects of the following variables must be considered :—

(1) Rate of sweating;
(2) Rate and extent of cooling of the wax or wax–oil mixture in the sweater prior to commencing the sweating operation;

* Paper received 21st November, 1940.

(3) Amount of oil in the wax-oil mixture;
(4) Viscosity of the oil.

The process may be operated in different ways: a uniform temperature increase may be employed throughout the sweating operation; a period of gradual temperature rise may be combined with periods of constant temperature at different stages; the rate of temperature increase may be so regulated that the amount of liquid product collected in a given time remains constant for the duration of the experiment.

A consideration of the above methods of operation in conjunction with the design of the laboratory sweating apparatus indicated that the last method was the most likely to lead to accurate control, and was therefore likely to give the most satisfactory comparative results.

Sweating Equipment.

Satisfactory sweating, besides being dependent on the nature of the wax, is especially sensitive to the adequate control and regulation of temperature throughout the system, and to an adequate means of draining the liquid formed during the operation. It was believed that an electrically heated sweater of the stove type would be most likely to fulfil these requirements in laboratory scale-experiments.

The sweater finally employed consisted essentially of a cage in which the wax was supported, fitted with a series of internal heating coils and also a surrounding external heater. The component parts are shown in Fig. 1. The cage *A* is a cylinder of length 6½ inches, diameter 3¼ inches, open at one end, and made from perforated brass sheeting having forty-two perforations (of diameter $\frac{7}{64}$ inch) to the square inch. The spacer or carrier *B*, which fits into the open end of the cage, consists of two circular brass discs 1½ inches apart. Each disc contains three small holes for the insertion of thermometers, and nineteen holes each of diameter ⅜ inch arranged symmetrically over the disc. The chief function of the spacer is to maintain the nineteen internal heaters *C* evenly spaced in the cage, this even spacing of the heaters being essential in order to secure a uniform distribution of the heat throughout the wax mass in the sweater. Each of the internal heaters consists of an outer glass tube of length 7½ inches and diameter $\frac{5}{16}$ inch, sealed at one end, which contains the heating element comprising 2 feet 6 inches of resistance wire (resistance 1·08 ohms per foot), supported on a length of glass tube of considerably smaller diameter.

A thickness of asbestos paper was placed between the heater and the external glass tube, and a small amount of asbestos powder was placed in the bottom of this tube. The heating elements were joined in series with small terminal connections.

The internal heating tubes, supported in the spacer, made contact with the bottom of the cage when placed in position in the latter. The set-up of the sweater when ready for use is shown in Fig. 2. The external heater (not shown) consisted of an iron sheet welded into the form of a hollow cylinder of length 10½ inches and diameter 4¼ inches. The outer surface was covered with a layer of asbestos on which was wound the heating element, which, in turn, was covered with a thicker layer of asbestos.

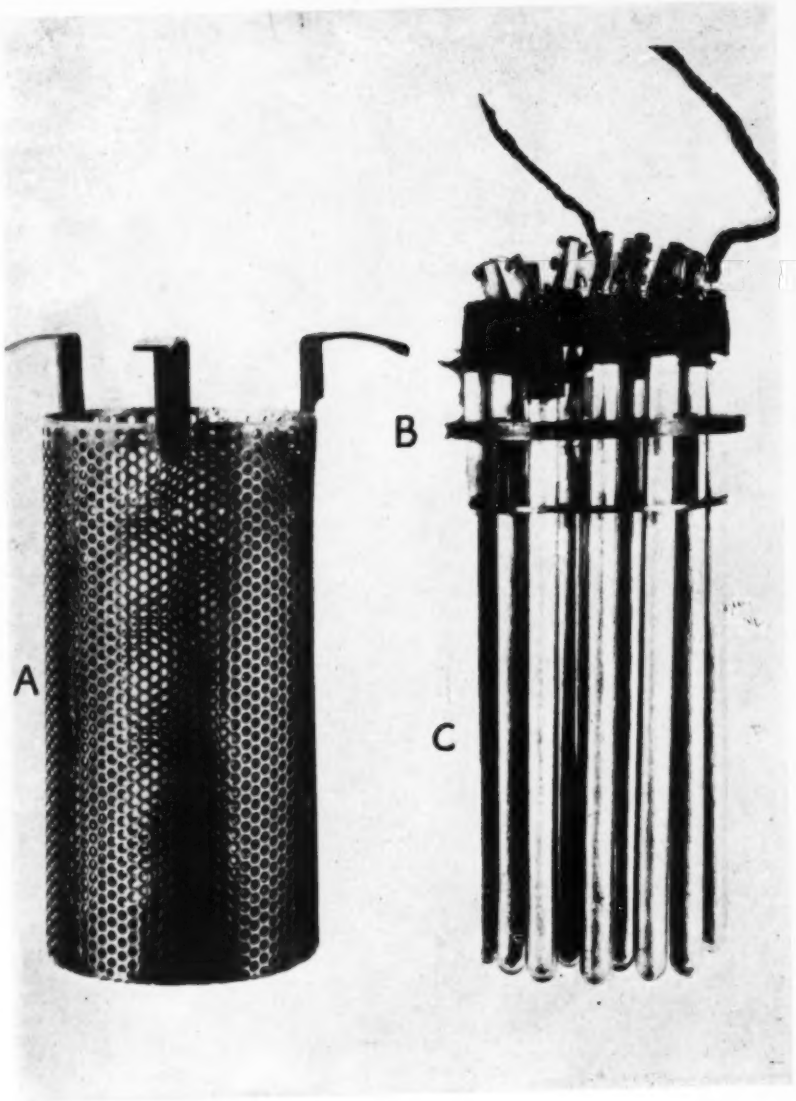

FIG. 1.

[*To face p.* 2.

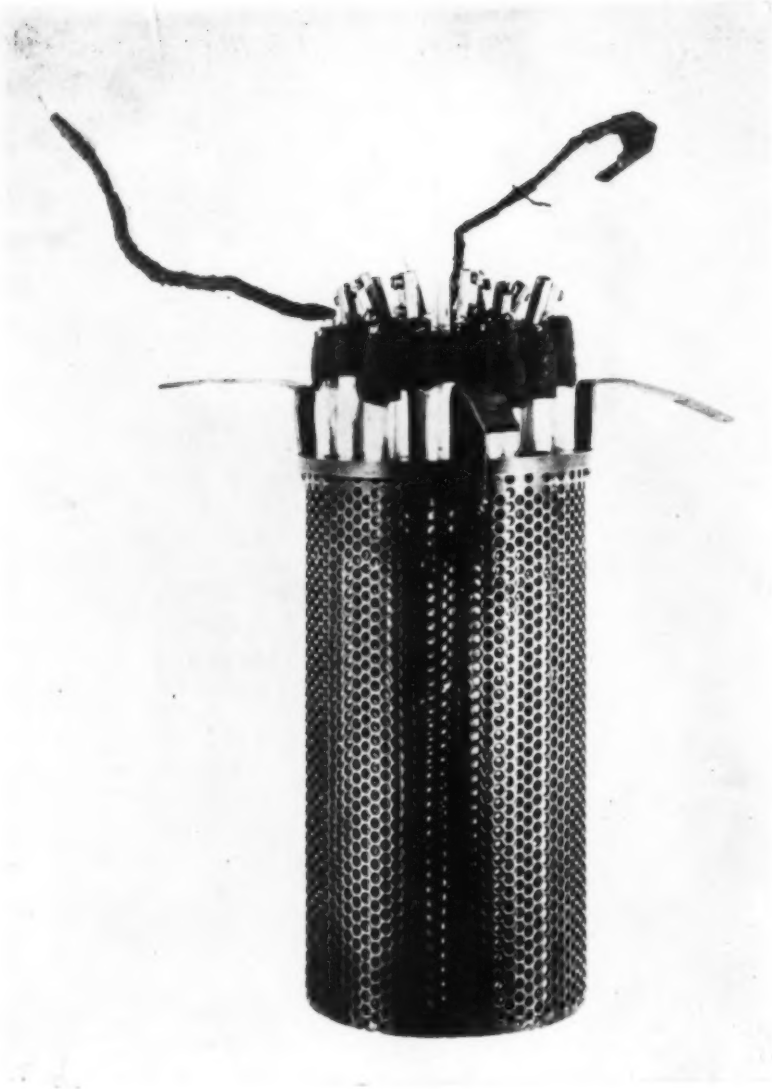

FIG. 2.

After this work had been in progress for some time it was found that a laboratory sweater of similar construction had been previously developed by the Research Staff of the Burmah Oil Company.

Experimental Procedure.

The following method of preparing the sample was found to be very satisfactory. The outer surface of the sweater was completely covered with a sheet of cellophane held tightly against the surface by means of a number of rubber bands. Additional support was afforded the cellophane covering the bottom of the sweater by placing the latter in a suitable tin-lid containing a small amount of molten wax; the wax was solidified by placing the bottom of the apparatus in cold water. In order to heat the glass containing the internal heating elements, current was passed through the latter for a short period, after which the molten wax sample, which had been maintained at a temperature 15–20° F. above its melting point, was introduced into the apparatus through a glass filter funnel inserted into one of the thermometer holes in the spacer. The cage was filled to within $\frac{1}{2}$ inch below the lower plate of the spacer, the capacity being approximately 440 grams of wax. The sweater and its charge were then placed in a position away from draughts and allowed to cool under any desired conditions. Cooling of the mass to room temperature normally occupied about 6 hours. At the end of this period the lower portion of the apparatus was momentarily placed in warm water to loosen the wax adhering to the tin; the cellophane covering was then taken from the surface of the sweater and the very thin layer of wax partly covering the latter was removed.

For the actual sweating or fractional melting experiment the external heater was supported on a tripod in which was placed a glass filter funnel of diameter 4 inches (*i.e.*, of larger diameter than the sweater). A screen of asbestos paper was placed round the tripod. The sweater was supported in the centre of the external heater. During the experiment the liquid wax phase fell from the sweater into the filter funnel, and thence into any convenient collecting vessel. It was found, especially during the later stages of the experiment when the liquid phase consisted of waxes of comparatively high melting point, that the liquid tended to solidify in the filter funnel. This was prevented by maintaining a minute gas flame in a position between the beaker and one of the tripod legs—the warm air from the flame being deflected on to the filter funnel by means of a small sheet of tin held in a clamp.

The simple electrical heating arrangement employed is shown in Fig. 3, and is self-explanatory. There are two separate circuits :—

(1) *Internal heating*, comprising a variable resistance R_1, fixed resistances R_3 and R_4; ammeter A_1 (range 0–250 milliamp.); and the internal heating elements of the sweater; and

(2) *External heating*, comprising a variable resistance R_2, fixed resistances R_5 and R_6; ammeter A_2 (range 0–1 amp.); and the external heater.

Little difficulty was encountered in maintaining any desired rate of

sweating between 3 per cent. and 15 per cent. per hour, but at rates higher than 15 per cent. per hour the process tended to become unmanageable. With care and constant attention it was possible to limit the temperature gradient through the wax mass to 2–3° F. for oil-free waxes, and to 1° F. for waxes containing oil.

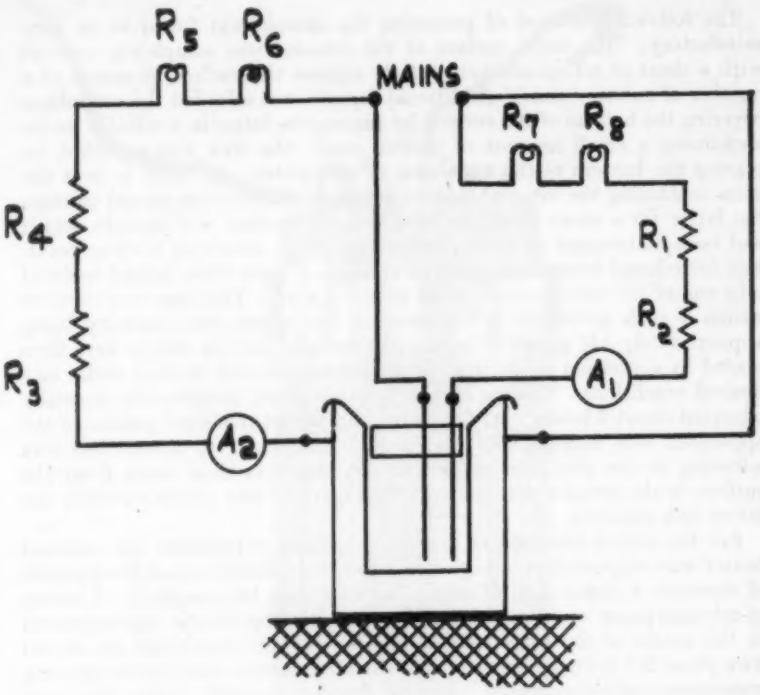

FIG. 3.

The external heating was regulated so that the air temperature in the space between the sweater and the external heater was within ± 0·5° F. of the temperature of the liquid dropping from the sweater.

EXPERIMENTAL STUDY OF THE FRACTIONAL MELTING OF OIL-FREE WAX.

Employing a given oil-free wax stock, two only of the variables previously mentioned have to be considered: the rate of sweating, and rate and extent of cooling of the wax prior to sweating. The time–cost factor is of obvious industrial importance, but this variable cannot receive consideration here.

The object of the sweating process is to remove oil, and to obtain as high a yield as possible of a satisfactory wax of some desired melting

point, and hence, in the absence of oil, the latter becomes the principal object.

For the purpose of investigating the effect of the rate of sweating on the yields of products, a series of experiments covering the range 3–20 per cent. per hour was made.

The wax stock, melting point 122·1° F., was that used in the determination of the wax equilibrium diagram,[2] and the sample used in each experiment was prepared according to the procedure already described, and then allowed to solidify over-night. The temperature of the wax mass was gradually increased from room temperature, over a period of 4–4½ hours, before the initial appearance of the liquid in the collecting vessel. From this stage the heating was arranged so that the fractional melting proceeded at the desired rate.

The first and, on occasion, the second fractions—representing a 5–10 per cent. yield were collected at a slightly slower rate, this precaution being taken to avoid the possibility of the experiment getting out of control in the early stages. By the time 10 per cent. of the stock had been collected, the fractional melting was proceeding at the desired rate.

When less than 5 per cent. of the stock remained in the sweater, the current passing through the internal and external heaters was increased, in order to facilitate the removal of this residue wax. The last traces were removed by supporting the sweater in an air oven maintained at a temperature of 150–160° F., and allowing the last drops to fall into the collecting vessel. The draining was assisted by occasionally shaking the apparatus, and, by following this procedure, the amount of wax finally remaining in the sweater was seldom more than 1 gram.

When the liquid phase was removed at rates of 10 per cent. per hour and higher, the experiment was completed in 1 day, but for rates of 5 per cent. and 3 per cent. per hour, 2 and 4 days, respectively, were required for the completion of the runs. During the first day of the 5 per cent. per hour runs, 50–60 per cent. of the wax was removed from the sweater, and that remaining in the apparatus was allowed to cool to room temperature over-night. On the second day the wax mass was slowly warmed over a period of 4½–5 hours before the initial drops of liquid phase were collected.

By careful regulation of the heating it was possible to control the rate to $\pm 0{\cdot}5$ per cent. per hour except in the 20 per cent. per hour run, where the rate was too high for accurate control.

A temperature gradient of 2–3° F. normally existed in the wax mass during the first half of the run when larger quantities of wax were present in the sweater. As the experiment progressed, however, this temperature gradient became smaller.

Difficulty was experienced in maintaining the desired rate during the fractionation of the last 10 per cent., owing to the comparatively small amount of wax present in the sweater at this stage. Any errors involved are, however, believed to be small and relatively unimportant.

The sweats were, in general, collected in cuts of 5–7 per cent. by weight, and the melting point of each fraction was determined in the manner previously described.[2]

In order to obtain the figures for a comparison of the relative efficiencies for the different rates of separation of the waxes, it is necessary to know

the yield and melting point of the residual wax present in the sweater at any given stage of the experiment. This may be found by :—

(*a*) Blending the fractions—starting with the last two collected—and determining the melting point of the blend after the addition of each two consecutive fractions ; or

(*b*) Calculation, employing the relationship $T = \frac{414{\cdot}5\,M}{M + 94{\cdot}4}$ as previously described.

Excellent agreement was found between experimental and calculated figures, as indicated in columns 8 and 9 of Table I, which gives the essential data obtained for the 3 per cent. per hour run.

TABLE I.

Experimental Run No. 8. Rate of Sweating, 3 per cent. per hour.

Fraction No.	Liquid phase.				Residue wax in sweater.			
	Wt., gms.	Yield, wt. % of stock.	M. pt., ° F.	Mol. wt.*	Yield, wt. %.	Mol. wt.*	M. pt. (calc.), ° F.	M. pt., ° F.
0	—	—	—	—	100·0	333·7	122·00	122·05
1	18·68	4·8	106·25	296·2	95·2	335·6	122·65	—
2	21·92	5·6	109·05	302·3	89·6	337·6	123·45	123·50
3	20·52	5·3	110·00	304·6	84·3	339·8	124·35	—
4	26·78	6·9	112·60	310·5	77·4	342·3	125·20	125·20
5	22·58	5·8	113·75	313·2	71·6	344·6	126·05	—
6	24·91	6·4	116·50	319·9	65·2	347·1	127·05	127·00
7	23·80	6·1	118·35	324·5	59·0	349·4	127·90	—
8	22·94	5·9	119·40	327·0	53·1	351·9	128·85	128·90
9	23·02	5·9	120·20	329·2	47·2	354·8	129·90	—
10	23·16	6·0	121·10	331·5	41·3	358·2	131·10	131·20
11	23·11	5·9	123·35	337·3	35·3	361·7	132·30	—
12	26·28	6·8	125·75	343·7	28·6	365·9	133·80	133·80
13	26·60	6·8	127·05	347·1	21·7	371·8	135·75	—
14	22·92	5·9	130·45	356·5	15·8	377·7	137·70	137·75
15	27·47	7·1	133·65	365·5	8·8	387·5	140·65	—
16	13·08	3·4	137·30	376·5	5·4	394·2	142·70	142·70
17	20·62	5·4	142·70	394·2	0·0	—	—	—

* Calculated from the relation $T = \frac{414{\cdot}5\,M}{94{\cdot}4 + M}$.

The respective yield/melting-point graphs for the 3 per cent. per hour run and the 14-stage equilibrium experiments [2] are shown in Fig. 4, and although the curves are of a similar form, it will be noted that for a given melting point the yield of wax is higher in the actual sweating process than in the multi-stage equilibrium experiments. This finding does not, however, affect in any way the theory developed in connection with the equilibrium diagram, but rather emphasizes the experimental difficulties involved in its determination. It is clear that, at least in respect to yields, the actual sweating experiment represents a nearer approach to the ideal or infinite-stage process than does the equilibrium experiment.

In the multi-stage equilibrium experiments it was found that the melting point of the liquid phase was, in general, 0·2–0·3° F. lower than the equilibrium temperature. It is therefore of interest to compare the melting points of the individual fractions obtained in the 3 per cent. per hour run

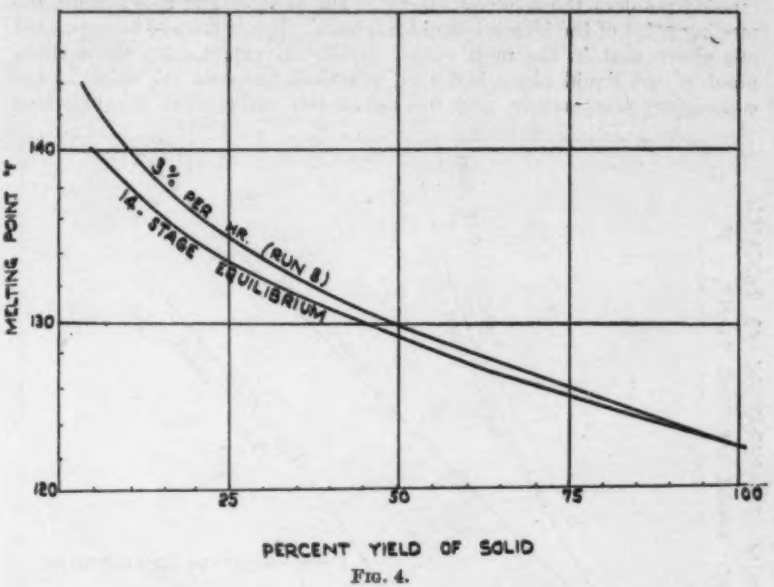

FIG. 4.

with the temperature at which they left the sweater. The relevant figures are given in Table II.

TABLE II.

Fraction No.	Melting point, ° F.	Temperature of wax at end of cut, ° F.	Difference in temperature, ° F.
1	106·75	112·7	5·9
2	109·05	114·8	5·7
3	110·00	117·3	6·3
4	112·60	118·0	5·4
5	113·75	118·6	4·8
6	116·50	120·0	3·5
7	118·35	121·9	3·5
8	119·40	124·2	4·8
9	120·20	124·8	4·6
10	121·10	126·0	4·9
11	123·35	128·0	4·6
12	125·75	129·6	3·8
13	127·05	132·4	5·3
14	130·45	135·0	4·5
15	133·65	139·0	5·4
16	137·30	144·0	6·7
17	142·70	—	—

The difference is considerable, and is probably due to drainage lag.

In Fig. 5 the equilibrium diagram for the 14-stage process is compared with the diagram resulting when the data obtained in the 3 per cent. per hour run are plotted in the same way. The equilibrium temperature, taken as the melting point of the liquid fraction, is plotted against the melting point of the solid remaining in the sweater and also against the melting point of the blended liquid fractions. It has already been pointed out above that in the multi-stage equilibrium experiments the melting point of the liquid phase is for all practical purposes the same as the equilibrium temperature, and the use of this rather than the indicated

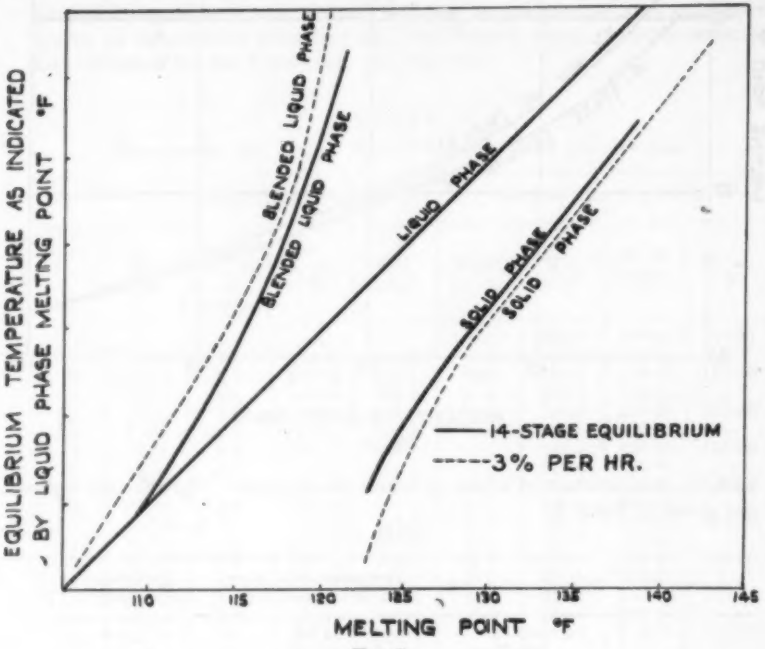

FIG. 5.

temperature at which the liquid fraction left the sweater is to be preferred. As will be seen from this figure, the two diagrams are closely similar. The 3 per cent. per hour run represents a nearer approach to the ideal infinite-stage process than does the multi-stage equilibrium experiment.

It is probable that the difference between the two diagrams is due to the difference between a 14-stage and an infinite-stage process. If the 14-stage equilibrium experiment could have been replaced by 30- or 40-stage equilibrium experiments, then the resulting diagrams would probably have been even nearer the ideal process diagram. It is clear from Fig. 5 that the previously derived conception of the sweating process is a true one, and that an equilibrium diagram based on the results of static experiment with a large number of stages could be used as a basis for computing

sweating efficiency. In view, however, of the difficulty of carrying out such an experiment, it is suggested that the diagram obtained at a low rate of sweating—say, 3 per cent. per hour or less—in an experimental sweater such as that described in this paper, be used for this purpose.

The melting point/refractive index (n_D^{60}) relationship for the single fractions collected in the 3 per cent. per hour run is of special interest when compared with the corresponding relationship for the *n*-paraffins. The lower curve in Fig. 6 is plotted from the following values of n_D^{60} for pure *n*-paraffins taken from various sources.

TABLE III.

Refractive Index of n-*Paraffins.*

Carbon atoms in molecule.	Melting point, ° C.	Melting point, ° F.	n_D^{60}.
21	40·5	104·9	1·4287
22	44·4	111·9	1·4305
23	47·7	117·9	1·4319
24	51·1	124·0	1·4323
25	53·8	128·8	1·4341
26	56·6	133·9	1·4355
27	59·5	139·1	1·4366
28	62·0	143·6	1·4375

The value of n_D^{60} for each of the wax fractions was determined at 60° C. with an Abbé Refractometer. The values for fractions of melting point

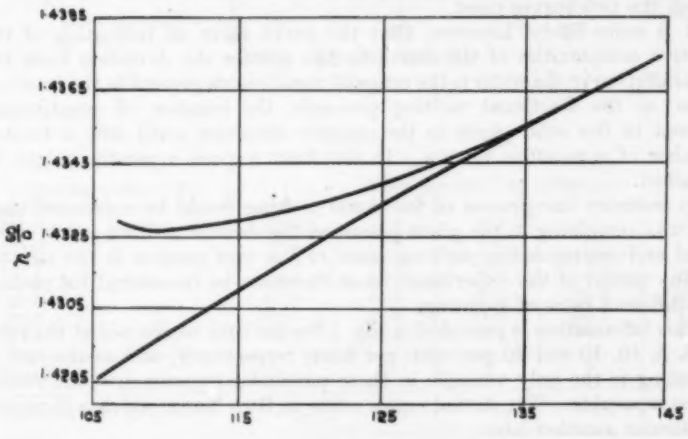

FIG. 6.

higher than 60° C. were determined at a temperature 1° C. above the respective melting points, and a correction factor of 0·0004 per 1° C. applied to obtain the equivalent value of n_D^{60}. The figures for n_D^{60} given in Table IV, from which the upper curve of Fig. 6 is plotted, are correct to ± 0·0001.

TABLE IV.

Fraction No.	Melting point, ° F.	n_D^{60}.	Fraction no.	Melting point, ° F.	n_D^{60}.
1	106·25	1·4331	9	120·20	1·4336
2	109·05	1·4327	10	121·10	1·4337
3	110·00	1·4328	11	123·35	1·4339
4	112·60	1·4328/9	12	125·75	1·4342
5	113·75	1·4330	13	127·05	1·4344
6	116·50	1·4332	14	130·45	1·4349
7	118·35	1·4333	15	133·65	1·4354
8	119·40	1·4334/5	16	137·30	1·4362
			17	142·70	1·4373/4

The curve for the wax is initially displaced from the corresponding *n*-paraffin curve, but approaches the latter as the melting point of the fraction increases. The two curves meet at the point representing Fraction No. 15, and then become almost coincident. The value of n_D^{60} for the first fraction is higher than for the second, an anomaly that may be explained by the presence in the first fraction of the small amount of oil originally present in the wax stock.

Two possible explanations may be advanced to account for the nature of the curve for the wax fractions.

The values of n_D^{60} for *iso*paraffins are considerably higher than for *n*-paraffins of the same melting point. It is therefore possible that the wax contains *iso*paraffins which are gradually removed during the process of fractional melting until removal is complete at Fraction 15, the stage at which the two curves meet.

It is more likely, however, that the curve gives an indication of the relative complexities of the fractions, the greater the deviation from the *n*-paraffin curve the wider is the range of constituents present in the fraction. Thus, as the fractional melting proceeds, the number of constituents present in the solid phase in the sweater decreases until only a limited number of *n*-paraffins remain. In the limit a pure *n*-paraffin might be obtained.

In industry the process of fractional melting would be continued until the wax remaining in the plant possessed the desired melting point. The yield and corresponding melting point of the wax present in the sweater at any period of the experiment must therefore be considered for each of the different rates of sweating.

This information is provided in Fig. 7 for the runs conducted at the rates of 3, 5, 10, 15 and 20 per cent. per hour, respectively, and as the rate of sweating is the only variable in these particular experiments, the results are comparable. The dotted curve refers to Run No. 4, which will receive particular mention later.

The yields of waxes of various melting points obtained from the curves in Fig. 7 are given in Table V for each of these runs.

For rates of 10 per cent. per hour and higher the yields of wax when less than 10 per cent. should be accepted with some reserve, as they are probably too high, owing to the difficulty experienced in maintaining the high rate of sweating with only a small amount of wax remaining in the sweater.

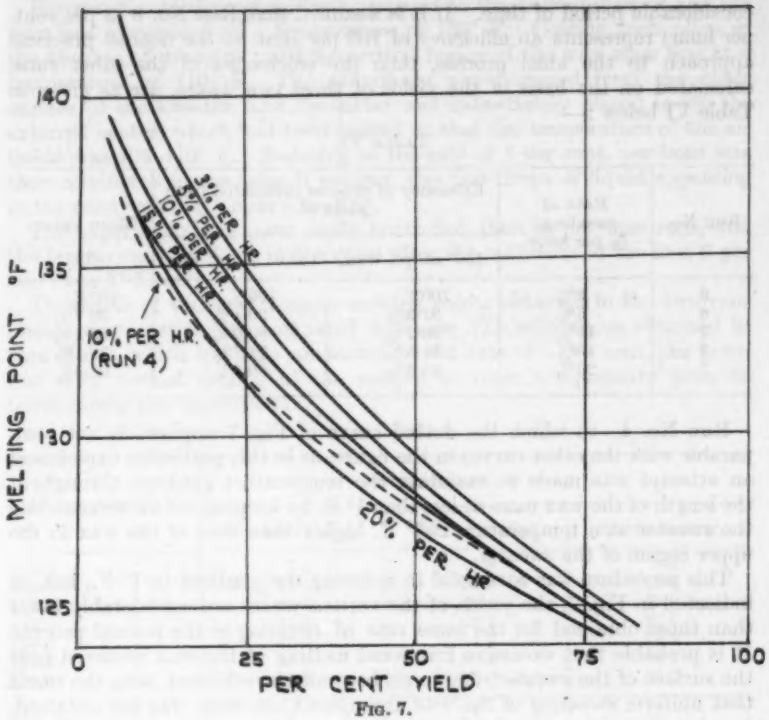

FIG. 7.

TABLE V.

Melting point, ° F.	Yield per cent. (by weight).				
140·0	10·4	7·4	3·0	—	3·1
137·5	16·5	13·5	8·8	7·0	7·0
135·0	24·2	21·2	17·2	14·8	13·1
132·5	34·4	31·0	27·5	25·7	20·5
130·0	47·0	42·9	40·5	38·3	30·8
127·5	61·5	58·0	54·8	55·2	47·5
125·0	78·8	75·8	74·3	75·0	69·8
Run No. . . .	8	6	3	2	7
Sweating rate (per hour).	3%	5%	10%	15%	20%

It is clear from the data contained in Table V that the yield of wax of a given melting point decreases with increase in the rate of sweating. The yields of 130° F. and 132·5° F. melting-point waxes may be taken as a satisfactory basis for the estimation of the relative efficiencies at the different rates, as these waxes are present in the sweater in each experiment at a stage when the sweating has been proceeding at the desired rate for a

considerable period of time. If it is assumed that Run No. 8 (3 per cent. per hour) represents an efficiency of 100 per cent. as the nearest practical approach to the ideal process, then the efficiencies of the other runs, calculated on the basis of the yields of these two waxes, are as given in Table VI below :—

TABLE VI.

Run No.	Rate of sweating, % per hour.	Efficiency of process calculated from yield of :		Mean value.
		130° m. pt. wax.	132·5° m. pt. wax.	
8	3%	100%	100%	100%
6	5%	91·3%	90·1%	90·7%
3	10%	86·2%	80·0%	83·1%
2	15%	81·5%	74·7%	78·1%
7	20%	65·5%	59·6%	62·5%

Run No. 4—to which the dotted curve of Fig. 7 applies—is not comparable with the other curves in the figure, as in this particular experiment an attempt was made to maintain the temperature gradient throughout the length of the wax mass at less than 1° F. by keeping the air surrounding the sweater at a temperature 2–3° F. higher than that of the wax in the upper region of the sweater.

This procedure was successful in reducing the gradient to 1° F., but, as indicated in Fig. 7, the yields of the various waxes are considerably lower than those obtained for the same rate of sweating in the normal process. It is probable that excessive fractional melting of the wax occurred near the surface of the sweater, due to its becoming overheated, with the result that uniform sweating of the wax throughout the mass was not obtained. Local overheating therefore has an adverse effect on the yields of the various waxes.

EFFECT OF METHOD OF PREPARATION OF SAMPLE PRIOR TO SWEATING.

Two experiments—runs 10 and 11—were conducted for the purpose of investigating the extent to which the efficiency of the process is dependent on the method of preparing the wax sample prior to sweating.

In run No. 10 the sweater was prepared in the normal manner and the wax was introduced at a temperature of 135–140° F. The sweater and contents were immediately plunged into an acetone–solid CO_2 mixture at −55° C. The acetone was maintained at a temperature of −50 to −55° C. during the solidification of the wax, which was complete in 35 minutes. After solidification, the wax temperature fell at the rate of 3° F. per minute, and when the central region of the mass had cooled to 50° F., the sweater was removed from the acetone bath. The sample remained at room temperature over-night, and sweating at the rate of 5 per cent. per hour was commenced on the following day.

During the early stages of the run some difficulty was experienced in keeping the temperature gradient of the wax mass within 3° F., but the run proceeded normally after the collection of the initial 10 per cent.

For run No. 11 the sweater was prepared in the normal manner and the wax was introduced at a temperature of 135° F. Cooling took place in the absence of draughts until the central region of the wax mass was at a temperature of 110° F. The cellophane was removed from the outer surface of the sweater, and the latter was immediately placed inside the external heater, which had been heated so that the temperature of the air inside was 105–110° F. Sweating at the rate of 5 per cent. per hour was then conducted in the normal manner, the first drops of liquid appearing in the receiver after 1 hour's heating.

The experiment was more easily controlled than in previous runs, and the temperature gradient in the mass after the collection of the first 5 per cent. was 1° F. only.

The yields of waxes of various melting points obtained in the two runs under consideration are compared in Table VII with those obtained in Run No. 6, which was also conducted at the rate of 5 per cent. per hour, but after normal cooling of the sample to room temperature prior to commencing the experiment.

TABLE VII.

Melting point, ° F.	Yield, per cent. by weight.		
	Normal cooling.	Partial cooling.	Shock cooling.
140·0 . . .	7·4	6·8	6·2
137·5 . . .	13·5	12·0	12·0
135·0 . . .	21·2	18·8	18·0
132·5 . . .	31·0	28·7	27·6
130·0 . . .	42·9	41·7	39·2
127·5 . . .	58·0	57·4	54·0
125·0 . . .	75·8	75·0	73·2
Run No. . .	6	11	10
Rate . . .	5% per hour	5% per hour	5% per hour

The yields of the various waxes obtained in Runs 6 and 11 are very similar, and it appears that only a slight advantage is to be gained by cooling to room temperature before commencing to sweat. It is likely that this slight increase in yield would be more than balanced in the industrial operation by the increased cost involved in the additional cooling and heating required.

The difficulty experienced in the early stages of Run No. 10 in reducing the temperature gradient in the wax mass to the normal figure is reflected in the small yields of the lower-melting-point waxes. It is probable that the shock cooling promotes the formation of very small crystals—particularly in the surface region of the wax—which are not conducive to easy sweating, especially in the early stages.

SUMMARY.

The principal deductions from the fractional melting separation of waxes of different melting points from an oil-free wax stock may be summarized as follows :—

(1) The melting point–equilibrium temperature diagram obtained in the previously described [2] 14-stage equilibrium experiments is closely similar to that obtained at a low rate of sweating—3 per cent. per hour—in an experimental sweater. The data from the experimental sweater, worked at low rates, represent a nearer approach to the ideal infinite-stage process than that from the multi-stage equilibrium experiment. It is suggested that the diagram obtained at rates of 3 per cent. per hour or less in an experimental sweater, such as that described in this paper, be used as a basis for computing sweating efficiency.

(2) The rate of melting is a very important variable, and the efficiency of the process decreases with increase in the rate at which the process is conducted.

(3) Preparation of the sample by shock cooling to room temperature results in a wax mass which is more difficult to sweat during the early stages of the process.

(4) Cooling the sample to a temperature slightly below the complete solidification point, instead of to room temperature, before commencing the melting process results in a mass which is considerably easier to control during the early stages of the run. As the yields of the products are only very slightly lower than those obtained when the mass is cooled to room temperature, it may be concluded that the more extensive cooling is uneconomical, and therefore unnecessary.

(5) Local overheating, even to the extent of 2–3° F., has an adverse effect on the yields of the various waxes.

References.

[1] Sawyer, Hunter, and Nash, *J. Inst. Petrol.*, 1940, **26**, 390.
[2] *Idem, ibid.*, 1940, **26**, 430.

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THE IMPROVEMENT OF MIXED CRESOLS FOR INHIBITOR PURPOSES: THE USE OF MESITOL AS A GUM INHIBITOR.*

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SUMMARY.

Since the problem of improving mixed cresols as gum inhibitors consists in increasing the number of *ortho*- and *para*-alkyl substituents, a method for the synthesis of mesitol from commercial cresols has been investigated and shown to be possible, although experimental variables have not been worked out. It has been shown by direct comparison at various concentrations that mesitol has six times the efficiency of *o*-cresol as a gum inhibitor on a weight-to-weight basis.

EGLOFF, Morrell, Lowry and Dryer (*Industr. Engng Chem.*, 1932, **24**, 1375) have shown that *ortho*- and *para*-alkyl substitution increases the efficiency of a phenol as an inhibitor of gum formation in cracked spirits. The problem of improving the mixed cresols for inhibitor purposes is therefore the problem of increasing the number of *ortho* and *para* substituents in the cresol molecule. This may be carried out in a variety of ways. Thus B.P. 431,945 (1936, E.I. du Pont de Nemours) records the condensation of phenols with aldehydes in presence of sulphuric acid, whilst U.S. 2,058,881 (1937, Universal Oil Products) covers the product of reaction of olefins from cracked oil with a wood-tar distillate.

U.S. 2,061,111 (1937, Gulf Oil Co.) relates to the inhibitor produced by reacting cracked distillate with phenols in presence of sulphuric acid, and U.S. 2,149,759 (1939, Gulf Oil Co.) covers the use of the products of alkylation of phenols by refinery gases containing olefins in the presence of a small proportion of sulphuric acid.

It appeared to us that mesitol (2 : 4 : 6-trimethylphenol) would be a very efficient inhibitor, since it has both the *ortho* positions and the *para* position substituted by methyl radicals. Accordingly, mesitol was synthesized in the usual manner and its effect as an inhibitor of gum formation in Iranian cracked spirit compared with that of *o*-cresol by an accelerated oxidation test.† The results are shown in Fig. 1, from whence it is seen that mesitol has an efficiency of six times that of *o*-cresol on a weight-to-weight basis.

Although mesitol possesses many advantages over the mixed cresols, such as less solubility in water, and, being a colourless solid, is more easy to handle than the oily mixtures obtained by alkylation processes, it compares most unfavourably in price with the cresols, and a cheaper method of obtaining it was looked for. In the course of the investigation the following interesting observations were made and have been recently briefly reported in *Chemistry and Industry* (Kennedy, 1940, **59**, 297). The method investigated was an adaptation of the method of Caldwell and

* Paper received 1st June, 1940.

† A modification of that of Hunn, Fischer and Blackwood (*S.A.E.J.*, 1930, **26**, 34), which will be described in a later paper.

Thompson (*J. Amer. chem. Soc.*, 1939, **61**, 765), who hydrogenated the *ortho*-dimethylaminomethyl derivative of *sym.*-metaxylenol prepared according to Decombe (*Compt. rend.*, 1933, **196**, 866) by the combined action of dimethylamine and formalin on the phenol. In the presence of copper chromite catalyst (Adkins, Conner, and Folkers, *J. Amer. chem. Soc.*, 1932, **54**, 1145) in dioxan solution at 165° C. and at a pressure of hydrogen of 2600 lb. a yield of 58·5 per cent. of 2 : 3 : 5-trimethylphenol was obtained.

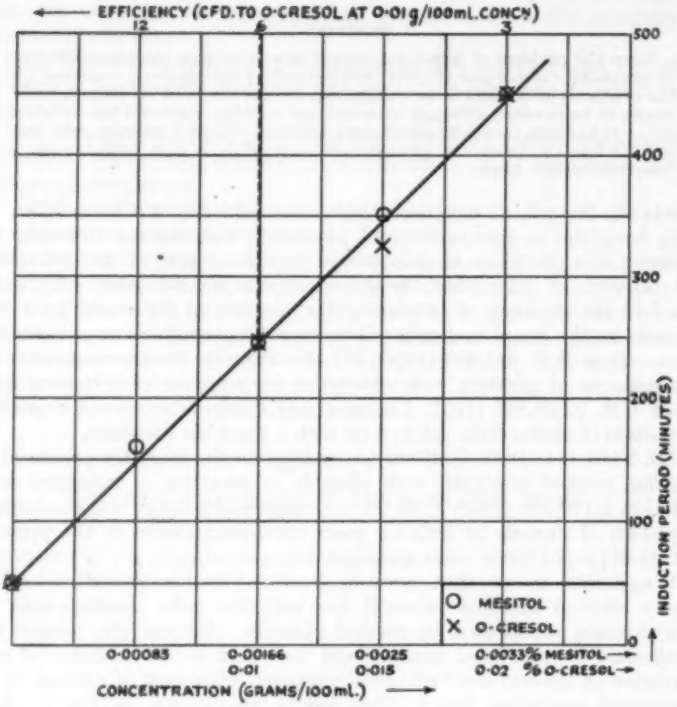


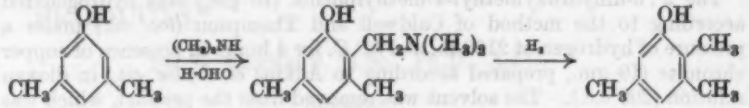
FIG. 1.

We have omitted the use of dimethylamine, and have used this reaction for the introduction of *two* methyl groups into the phenol molecule by the use of a compound which is obtained in almost theoretical yield from *p*-cresol, and which was first synthesized by Allmann and Buttner (*Ber.*, 1909, **42**, 2540) by the addition of two molecules of formaldehyde to an alkaline solution of the cresol.

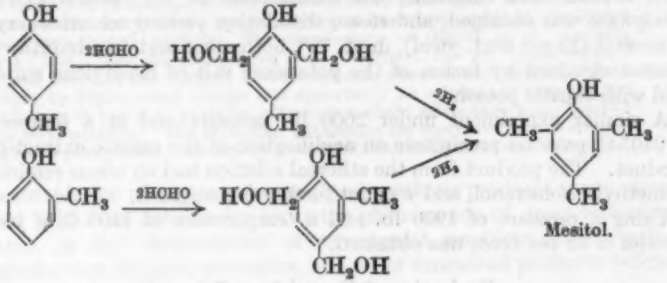
It was only possible to investigate the hydrogenation of this compound under very few conditions of temperature and pressure before the outbreak of war, but a yield of 25 per cent. of pure mesitol (m.pt. 70°) was obtained in 4 hours in presence of copper chromite in dioxan solution at a temperature of 170° C. and at a pressure of hydrogen of 2100 lb. Lowering of the temperature to 140° C. gave a yield of 10 per cent. of mesitol at 1900 lb.

pressure, whilst at a higher temperature (240° C.) and 2600 lb. pressure the benzene ring had apparently been hydrogenated, since no product soluble in caustic soda was obtained; the neutral residue had the very characteristic odour of methyl*cyclo*hexanol, and was undoubtedly mainly trimethyl*cyclo*hexanol.

DIAGRAM I.



Caldwell and Thompson.



It was only possible to try one set of conditions for the mixed cresols. In this case the crude product from the reaction of two moles of formaldehyde and a commercial mixed cresol was hydrogenated at a temperature of 180° C. and a pressure of 1800 lb. A yield of 2 per cent. of mesitol was obtained. It is readily seen from Diagram I that both *ortho* and *para* cresols will give mesitol by this series of reactions, and there appears to be no reason to doubt that the latter compound could be obtained in quantitative yield from mixed cresols by this method, but the variables, pressure, temperature, type and volume of solvent, type and amount of catalyst all remain to be further investigated.

EXPERIMENTAL.

Addition of Formaldehyde to p-*Cresol.* 2 : 6-*Dihydroxymethyl*-4-*methylphenol.*

The method used was that of Allmann and Buttner (*loc. cit.*).

p-Cresol (108 gm. 1 mole) was dissolved in a solution of caustic soda (50 gm.) in water (200 c.c.) and an aqueous solution of formaldehyde (35 per cent., 215 c.c.) added. The mixture was left at room temperature for 4 days and the precipitated sodium salt filtered off. After another 4 days a further quantity was obtained, which was added to the first, and the whole acidified at 0° in an atmosphere of nitrogen by slow addition of a solution of acetic acid (10 per cent.). On warming, the mass dissolved, and on cooling, crystallized out in large colourless plates, which after further crystallizations from aqueous methanol, aqueous acetic acid, or ethyl acetate had m.pt. 130·5° (von Auwers, *Ber.*, 1907, **40**, 2531 gives

m.pt. 133°); yield 95 per cent. The dihydroxymethyl-*p*-cresol readily decolorizes in air, and prolonged boiling in solution yields insoluble polymerization products.

Hydrogenation.

Mesitol.

The 2 : 6-dihydroxymethyl-4-methylphenol (10 gm.) was hydrogenated according to the method of Caldwell and Thompson (*loc. cit.*) under a pressure of hydrogen of 2100 lb. at 170° C. for 4 hours in presence of copper chromite (10 gm., prepared according to Adkins *et al.*, *loc. cit.*) in dioxan solution (200 c.c.). The solvent was removed from the product, which was dissolved in ether and the ethereal solution washed with water and extracted with caustic soda solution. On acidification of the caustic extract a precipitate was obtained, and steam distillation yielded colourless crystals of mesitol (25 per cent. yield), m.pt. 70°, both alone and on admixture with mesitol obtained by fusion of the potassium salt of mesitylene sulphonic acid with caustic potash.

A similar experiment under 2600 lb. pressure and at a temperature of 240° C. gave no precipitate on acidification of the caustic extract of the product. The product from the ethereal solution had an odour reminiscent of methyl*cyclo*hexanol, and was not further investigated.

Using a pressure of 1900 lb. and a temperature of 140° C. a yield of mesitol of 10 per cent. was obtained.

Production of Mesitol from Tricresol.

The addition of formaldehyde was effected as for *p*-cresol, but after a week the whole mixture was acidified and the crude, coloured mixture of unchanged cresols and addition products was hydrogenated as before, at 1800 lb. pressure and 180° C. On working up the product as described above, a yield of 2 per cent. of pure mesitol was obtained.

Inhibition Tests by the Accelerated Oxidation Test.

Solution under test.	Inhibition period (mins.).
Neat cracked spirit	50
" " + 0·00083 gm./100 c.c. mesitol	160
" " + 0·00166 gm./100 c.c. mesitol	245
" " + 0·01 gm./100 c.c. *o*-cresol	245
" " + 0·0025 gm./100 c.c. mesitol	350
" " + 0·015 gm./100 c.c. *o*-cresol	325
" " + 0·0033 gm./100 c.c. mesitol	450
" " + 0·02 gm./100 c.c. *o*-cresol	450

Thanks are due to the Chairman of the Anglo-Iranian Oil Co., Ltd., for permission to publish these results.

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THE EFFECT OF ALKYL SUBSTITUTION ON THE EFFICIENCY OF PHENOLS AS INHIBITORS OF GUM FORMATION IN PETROLEUM PRODUCTS.*

By T. KENNEDY, M.Sc., Ph.D., A.I.C.

SUMMARY.

The effect of alkyl substitution on the efficiency of phenols as inhibitors of gum formation in cracked spirits has been more thoroughly investigated in the case of the six xylenols, and observations have been made on the higher methyl substituted phenols. The conclusions of Egloff *et al.* (*Industr. Engng Chem.*, 1932, **24**, 1375) have been confirmed, but an "*ortho* effect" has been noted in the cases of 1 : 5 : 6-xylenol, durenol, and mesitol. Substitution by higher-alkyl groups has apparently no advantage over methyl substitution in the *para* position, although a slight advantage was observed in the *ortho* position. The molecular efficiencies (as compared to the cresols) of eighteen phenols are recorded for gum inhibition in Iranian cracked spirits.

THE autoxidation of numerous natural and synthetic products on standing in air and light is an extensively occurring phenomenon of great economic importance, in that deterioration of commercial products often results by the production of gums, peroxides, and other unwanted products before use.

The problem of gum formation in petroleum products is generally held[1] to be due to the autoxidation of unsaturated hydrocarbons and the production of peroxides which may further decompose either at room temperature or on heating—*e.g.*, in an internal-combustion engine—to give gums. Before autoxidation commences, however, there is generally an induction period during which no peroxides are formed. Since petroleum products may have to be stored for a period before use, it is obviously advantageous to be able to increase this induction period by means of "inhibitors" of autoxidation.

The tendency of a product to form gum on standing may be assessed by noting the time taken by the product before appreciable oxidation occurs under standard conditions. A method in general use is that of Hunn, Fischer, and Blackwood[2] in which 200 c.c. of the oil are subjected to a pressure of 100 lb. per sq. in. of oxygen at a temperature of 100° C. in a bomb, and the time taken in minutes before a sharp drop in pressure is recorded, showing that the inhibition period is ended and that oxidation has set in, is taken as a measure of the efficiency of the inhibitor or of the potential gum-forming quality of the oil. Any comparison of efficiencies determined by this method will, of course, be a comparison at 100° C. and 100 lb. per sq. in. pressure of oxygen, and not at room temperature and pressure, but it is believed that this method does in fact give a good indication of the behaviour of the substance used as inhibitor under storage conditions. The efficiency of various gum inhibitors can be assessed by

* Paper received 1st June, 1940.

determining the "induction period" produced by a dilute solution of the inhibitor in the unstable liquid against a blank on an inhibitor of known efficiency.

Egloff, Morrell, Lowry, and Dryer [3] have studied the inhibitor action of a large number of substances on the autoxidation of a Pennsylvania cracked spirit in this manner, and found that modifying groups in amines and phenols were most effective in the *ortho* or *para* position, but that they exerted some beneficial influence when placed *meta* to the inhibiting group. They used a concentration of 0·01 gm. of inhibitor in 100 gm. of cracked spirit, and Table I gives the results they obtained on monohydric phenols.

Two alkyl groups were found to be more than twice as effective as a single group, and substitution in either *ortho* or *para* positions was considered to be nearly equivalent from a comparison of the four xylenols tested. They concluded that an *iso*propyl group *ortho* to the hydroxylic group is more effective than a methyl group, since thymol gave a longer induction period than carvacrol.

TABLE I.

Egloff et alii.[3]

Substance.	Induction period (min.).
Pennsylvania cracked spirit treated with fuller's earth	45
Phenol (0·01 gm. per 100 gm. spirit)	75
o-Cresol ,,	135
m-Cresol ,,	75
p-Cresol ,,	210
Butylphenol * ,,	195
tert.-Butylphenol * ,,	210
1 : 2 : 4-Xylenol ,,	420 §
1 : 2 : 6-Xylenol ,,	420 §
1 : 3 : 4-Xylenol ,,	255 §
1 : 2 : 5-Xylenol ,,	285
Thymol † ,,	300
Carvacrol ‡ ,,	180

* *ortho* and *para* mixed.
† 2-*iso*Propyl-5-methylphenol.
‡ 2-Methyl-3-*iso*propylphenol.
§ In benzene solution.

Because of the fact that the phenols isolated from petroleum fractions are often many times as efficient as the lower phenols, and since these "natural inhibitors" are in all probability simply mixtures of higher alkylphenols,[4] it was decided to investigate further the effect of alkyl substitution on inhibitor efficiency in the phenol series. The results reported below have been obtained in a similar manner to those of Egloff *et al.*, but using a smaller bomb (25 c.c. of cracked spirit). The bomb containing the sample in an open test-tube and connected to a recording pressure gauge was filled to a pressure of 100 lb. per sq. in. of oxygen and immersed in a steam bath. The steam was turned on and the time (T_1) noted. The pressure increased to a maximum due to increase in temperature, and remained steady for some time before dropping more or less sharply. The induction period was taken to be ($T_2 - T_1$), T_2 is the time at which the pressure has dropped to 2 lb. below the maximum pressure.

The spirit used was Iranian refined low-pressure cracked spirit, and a

fresh sample was taken each week and standardized against *o*-cresol. When not in use it was kept sealed, in a refrigerator at 0° C. The characteristics of a typical sample of this cracked spirit are given in Table II. Little variation was shown from week to week.

TABLE II.

Specific gravity	0·764/60° F.
Elemental sulphur	0·0002%
Sulphur content	0·024%
Doctor test	Negative
Colour 18 in. cell (Lovibond) I.P.T. series	Water white (1·0)
C.F.R. engine test (Octane No.)	69·5
I.B.P. (A.S.T.M. Distillation)	43° C.
10%	75·5° C.
50%	130° C.
90%	166·5° C.
F.B.P.	183° C.

The procedure in each case was to determine the induction period for one phenol at various concentrations between 0·0005 and 0·05 gm. per 100 c.c.

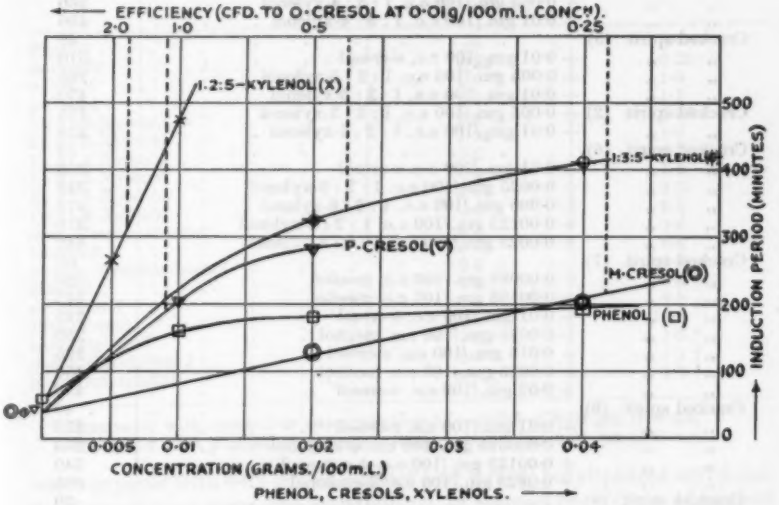


FIG. 1.

of cracked spirit, depending on the efficiency of the phenol. The induction period was plotted against the concentration of inhibitor and the concentration required to give an induction period equivalent to that given by 0·01 gm. of *o*-cresol read off. Then the efficiency of the phenol was taken to be 0·01 divided by the concentration read off from the graph. Molecular efficiencies were calculated by multiplying by the molecular weight of the phenol and dividing by the molecular weight of *o*-cresol. The results are given in Tables III and IV and are shown graphically in Figs. 1–7. There were two exceptions to the above procedure: *o*-amylphenol

TABLE III.

Substance.	Induction period (min.).
Cracked spirit (1)	60
" " + 0·01 gm./100 c.c. *o*-cresol	230
" " + 0·01 gm./100 c.c. phenol	160
" " + 0·02 gm./100 c.c. phenol	180
" " + 0·04 gm./100 c.c. phenol	195
Cracked spirit (2)	40
" " + 0·01 gm./100 c.c. *o*-cresol	215
" " + 0·02 gm./100 c.c. *m*-cresol	130
" " + 0·04 gm./100 c.c. *m*-cresol	200
Cracked spirit (3)	45
" " + 0·01 gm./100 c.c. *o*-cresol	190
" " + 0·01 gm./100 c.c. *p*-cresol	205
" " + 0·02 gm./100 c.c. *p*-cresol	280
Cracked spirit (4)	40
" " + 0·01 gm./100 c.c. *o*-cresol	340
" " + 0·02 gm./100 c.c. 1 : 3 : 5-xylenol	325
" " + 0·04 gm./100 c.c. 1 : 3 : 5-xylenol	410
" " + 0·005 gm./100 c.c. 1 : 3 : 4-xylenol	260
" " + 0·01 gm./100 c.c. 1 : 3 : 4-xylenol	490
Cracked spirit (5)	40
" " + 0·01 gm./100 c.c. *o*-cresol	310
" " + 0·005 gm./100 c.c. 1 : 2 : 5-xylenol	265
" " + 0·01 gm./100 c.c. 1 : 2 : 5-xylenol	470
Cracked spirit (2) + 0·005 gm./100 c.c. 1 : 2 : 3-xylenol	175
" " + 0·01 gm./100 c.c. 1 : 2 : 3-xylenol	255
Cracked spirit (6)	55
" " + 0·01 gm./100 c.c. *o*-cresol	355
" " + 0·0025 gm./100 c.c. 1 : 2 : 6-xylenol	340
" " + 0·005 gm./100 c.c. 1 : 2 : 6-xylenol	475
" " + 0·00125 gm./100 c.c. 1 : 2 : 4-xylenol	270
" " + 0·0025 gm./100 c.c. 1 : 2 : 4-xylenol	440
Cracked spirit (7)	50
" " + 0·00083 gm./100 c.c. mesitol	160
" " + 0·00166 gm./100 c.c. mesitol	245
" " + 0·01 gm./100 c.c. *o*-cresol	245
" " + 0·0025 gm./100 c.c. mesitol	350
" " + 0·015 gm./100 c.c. *o*-cresol	325
" " + 0·0033 gm./100 c.c. mesitol	450
" " + 0·02 gm./100 c.c. *o*-cresol	450
Cracked spirit (8)	40
" " + 0·01 gm./100 c.c. *o*-cresol	375
" " + 0·000625 gm./100 c.c. ψ-cumenol	205
" " + 0·00125 gm./100 c.c. ψ-cumenol	340
" " + 0·0025 gm./100 c.c. ψ-cumenol	665
Cracked spirit (9)	50
" " + 0·01 gm./100 c.c. *o*-cresol	355
" " + 0·000625 gm./100 c.c. *unsym.*-hemimellitenol	170
" " + 0·00125 gm./100 c.c. *unsym.*-hemimellitenol	245
" " + 0·0025 gm./100 c.c. *unsym.*-hemimellitenol	415
" " + 0·0025 gm./100 c.c. *sym.*-hemimellitenol	175
" " + 0·00375 gm./100 c.c. *sym.*-hemimellitenol	285
" " + 0·005 gm./100 c.c. *sym.*-hemimellitenol	405
Cracked spirit (10)	55
" " + 0·01 gm./100 c.c. *o*-cresol	370
" " + 0·00125 gm./100 c.c. durenol	250
" " + 0·0025 gm./100 c.c. durenol	430
" " + 0·000625 gm./100 c.c. prehnitenol	205
" " + 0·00125 gm./100 c.c. prehnitenol	395

TABLE III (*continued*).

Substance.	Induction period (min.).
Cracked spirit (11)	45
" " + 0·01 gm./100 c.c. *p*-cresol	220
" " + 0·01 gm./100 c.c. *p-tert.*-butylphenol	200
" " + 0·02 gm./100 c.c. *p-tert.*-butylphenol	290
" " + 0·02 gm./100 c.c. *p-iso*-octylphenol	205
" " + 0·04 gm./100 c.c. *p-iso*-octylphenol	430
Cracked spirit (12)	40
" " + 0·02 gm./100 c.c. *o*-cresol	200
" " + 0·02 gm./100 c.c. *o*-amylphenol	205
" " + 0·04 gm./100 c.c. *o*-amylphenol	315

TABLE IV.

	Efficiency compared with *o*-cresol at 0·01 gm./100 c.c. concentration.	Molecular efficiency.
Phenol	—	—
m-Cresol	0·25	0·25
o-Cresol	1·0	1·0
p-Cresol	1·1	1·1
1 : 3 : 5-Xylenol	0·5	0·55
1 : 2 : 3-Xylenol	1·35	1·5
1 : 3 : 4-Xylenol	1·5	1·7
1 : 2 : 5-Xylenol	1·6	1·8
1 : 2 : 6-Xylenol	4·0	4·5
1 : 2 : 4-Xylenol	6·0	6·8
sym.-Hemimellitenol	2·1	2·6
Durenol	5·0	6·9
unsym.-Hemimellitenol	5·5	6·9
Mesitol	6·0	7·6
ψ-Cumenol	7·0	8·8
Prehnitenol	8·0	11·1
o-Amylphenol	1·0 *	1·5 *
p-tert.-Butylphenol	0·8 †	1·1 †
p-iso-Octylphenol	0·5 †	1·0 †

* Compared with *o*-cresol at concentration of *o*-cresol of 0·02 gm./100 c.c.
† Compared with *p*-cresol at concentration of *p*-cresol of 0·01 gm./100 c.c.

was compared with 0·02 gm. of *o*-cresol and *p*-(*tert.*-butyl)phenol and *p-iso*-octylphenol were compared with 0·01 gm. of *p*-cresol per 100 c.c. of cracked spirit.

Of the phenols used in this investigation the following were obtained from the sources shown :—

Phenol	40–41° B.P. detached crystalline.	May and Baker.
o-Cresol	" Pure."	Hopkins and Williams.
p-Cresol	" " "	" "
m-Cresol	98–100%	British Drug Houses.
1 : 3 : 4-Xylenol	" Pure."	Gesel. für Teerverwertung.
1 : 2 : 4-Xylenol	" " "	" "
1 : 2 : 5-Xylenol	" " "	" "
1 : 3 : 5-Xylenol	"	Monsanto Chemicals, Ltd.
p-tert.-Butylphenol	"	" " "
o-Amylphenol	"	Sharples Solvent Corp., Philadelphia.

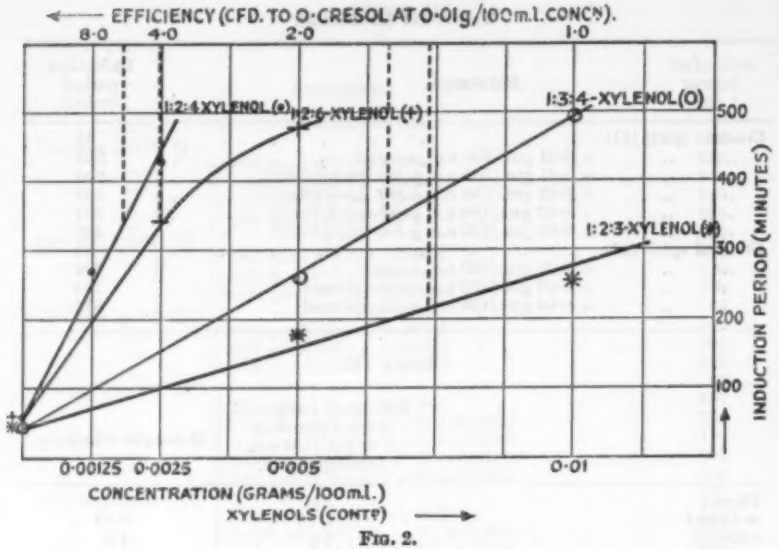

EFFICIENCY (CFD. TO O-CRESOL AT 0·01g/100m.l.CONCN).
8·0
4·0
2·0
1·0
1:2:4 XYLENOL (•)
1:2:5 XYLENOL (+)
1:3:4-XYLENOL (O)
1:2:3-XYLENOL (*)
500
400
300
200
100
INDUCTION PERIOD (MINUTES)
0·00125
0·0025
0·005
0·01
CONCENTRATION (GRAMS/100m.l.)
XYLENOLS (CONTD)

FIG. 2.

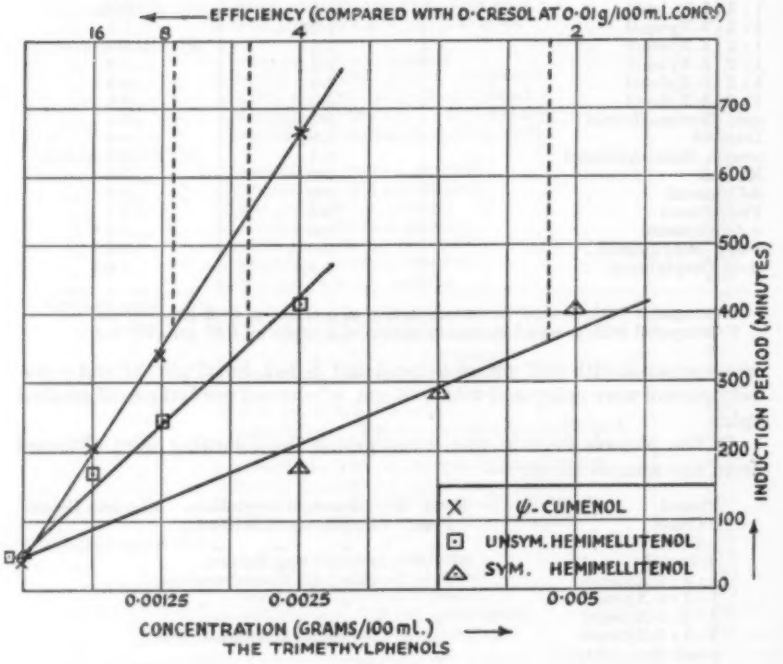

EFFICIENCY (COMPARED WITH O-CRESOL AT 0·01g/100 m.l.CONCN)
16
8
4
2
700
600
500
400
300
200
100
0
INDUCTION PERIOD (MINUTES)
X ψ-CUMENOL
UNSYM. HEMIMELLITENOL
SYM. HEMIMELLITENOL
0·00125
0·0025
0·005
CONCENTRATION (GRAMS/100 m.l.)
THE TRIMETHYLPHENOLS

FIG. 3.

1 : 2 : 6-Xylenol was obtained by Clemmensen reduction of 2-hydroxy-3-methylbenzaldehyde prepared from *o*-cresol by the method of Tiemann and Schotten.[5] The preparation of 1 : 2 : 3-xylenol presented much more difficulty. The method of Short, Stromberg, and Wiles,[6] a six-stage process starting by the nitration of *m*-cresol to 2-nitro-*m*-cresol and involving a Sandmeyer reaction on the corresponding amino-compound and a final Grignard stage, was thought to be unsuitable for the preparation of a small amount of this phenol, which was more readily prepared by the

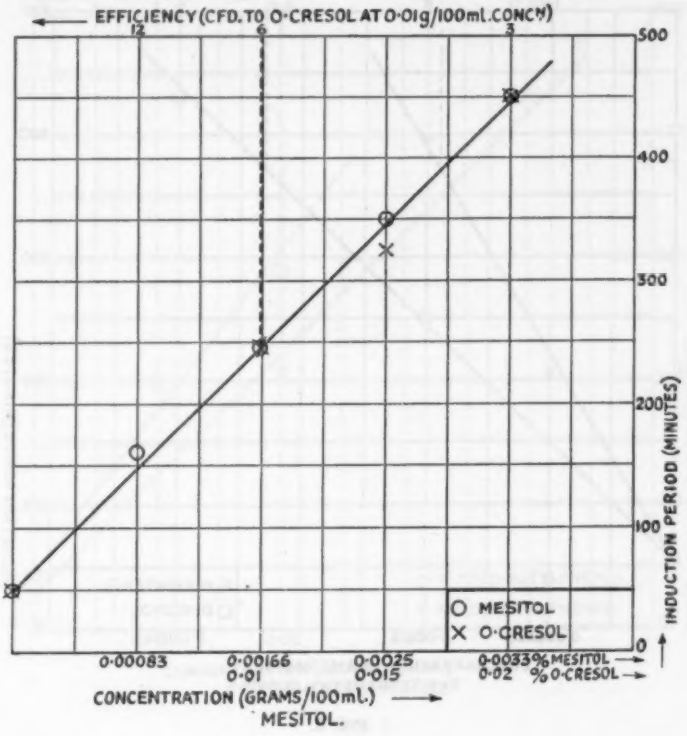


FIG. 4.

nitration of *o*-xylene,[7] reduction, separation of the 3-amino-*o*-xylene from the 4-amino-*o*-xylene by means of the formyl derivative,[8] and conversion of the amine by the action of nitrous acid into the corresponding 1 : 2 : 3-xylenol.

Mesitol, *ψ*-cumenol, *unsym.*-hemimellitenol, durenol, and prehnitenol were obtained by sulphonation of the corresponding hydrocarbons and fusion of the sodium salts of the sulphonic acids with caustic potash. Durene was prepared by the method of Smith [9] by methylation of xylenes. The residual

tetramethylbenzenes after removal of durene were subjected to the Jacobsen rearrangement [10] and prehnitene isolated from the product. *sym.*-Hemimellitenol was obtained by Clemmensen reduction of 2 : 6-dimethyl-4-hydroxybenzaldehyde; the latter compound was isolated in good yield from 1 : 3 : 5-xylenol by Gatterman's method. p-*iso*-Octylphenol was prepared acording to Niederl [11] from phenol and di*iso*butene.

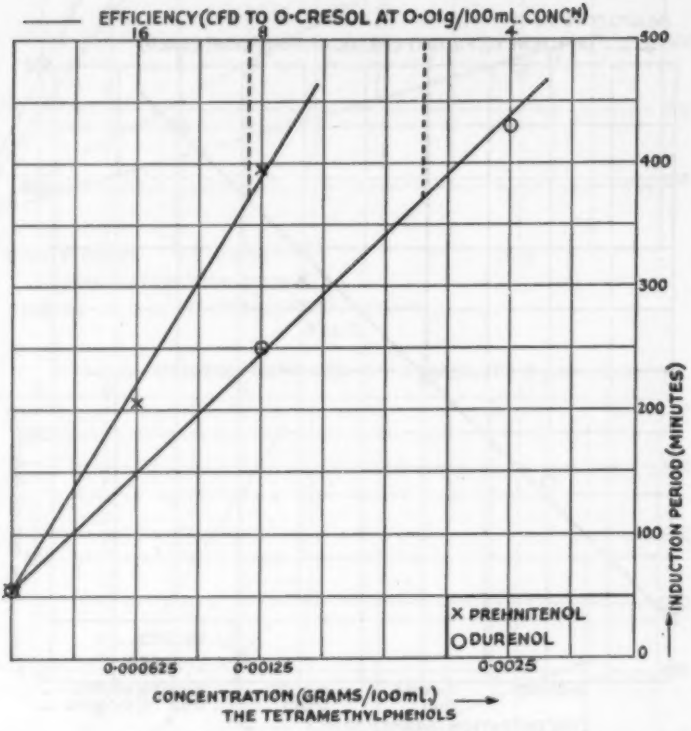


FIG. 5.

From the results certain conclusions may be reached. Thus since the efficiencies of *o*- and *p*-cresols are approximately the same and the efficiencies of 1 : 2 : 3-, 1 : 3 : 4-, and 1 : 2 : 5-xylenols are approximately the same, it is confirmed that the effects of *o*- and *p*-methyl groups are identical. It is also seen, as reported by Egloff, that when two methyl groups are present, the increase in efficiency is greater than would be expected from simple addition of the effects produced in the cresols. This is observed in 1 : 2 : 4-xylenol, where the combined effect of *o*- and *p*-substitution is much greater than the sum of the efficiencies of *o*- and *p*-cresol. This is

shown to be also true of the tri- and tetra-methylphenols. Thus substitution in the *meta*-position by a third methyl group in 1 : 2 : 4-xylenol to produce ψ-cumenol confers a far greater increase in efficiency than would be expected by simple addition of the efficiencies of *m*-cresol and 1 : 2 : 4-xylenol. This effect is not so noticeable when a *meta*-methyl group is the second substituent. Thus 1 : 3 : 5-xylenol has approximately the efficiency expected by simple addition and 1 : 2 : 3-, 1 : 3 : 4-, and 1 : 2 : 5-xylenols

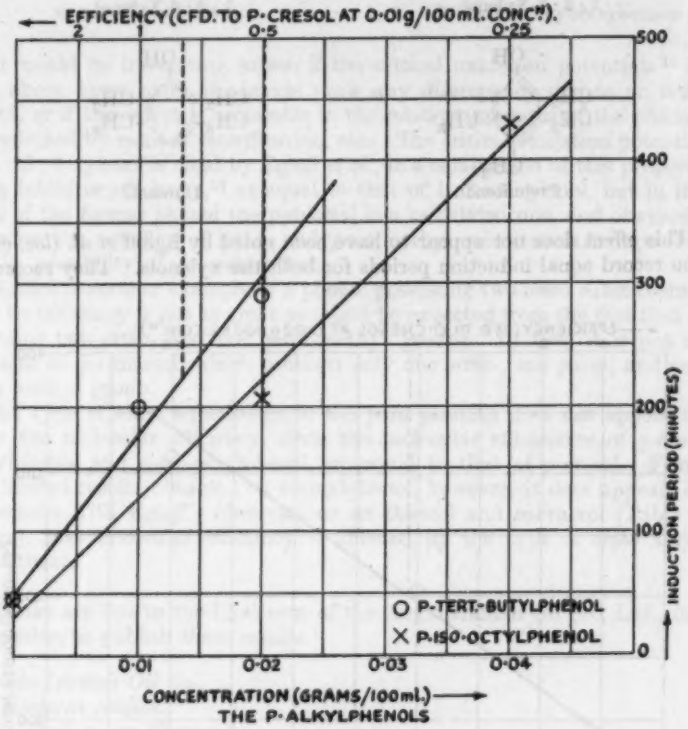
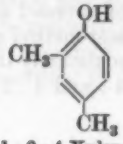


FIG. 6.

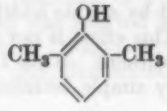
are not very much more efficient than would be expected by adding the efficiencies of the appropriate cresols. No explanation is offered of the difference in efficiency of *unsym.*-hemimellitenol and ψ-cumenol. It is noted, however, that 1 : 2 : 3-xylenol is similarly slightly less efficient than 1 : 2 : 5-xylenol.

The cases of durenol and 1 : 2 : 6-xylenol require special notice. It has been seen that the effect of *ortho*- and *para*-substitution was approximately equal in the cresols and xylenols, but the above two phenols possess an appreciably less efficiency than would be expected on comparison with

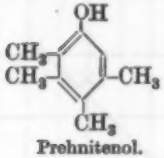
1:2:4-xylenol and prehnitenol respectively. It is obvious that we are here dealing with a typical "*ortho* effect."



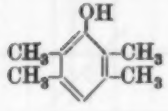
1 : 2 : 4-Xylenol.



1 : 2 : 6-Xylenol.



Prehnitenol.



Durenol.

This effect does not appear to have been noted by Egloff *et al.* (*loc. cit.*), who record equal induction periods for both the xylenols. They recorded

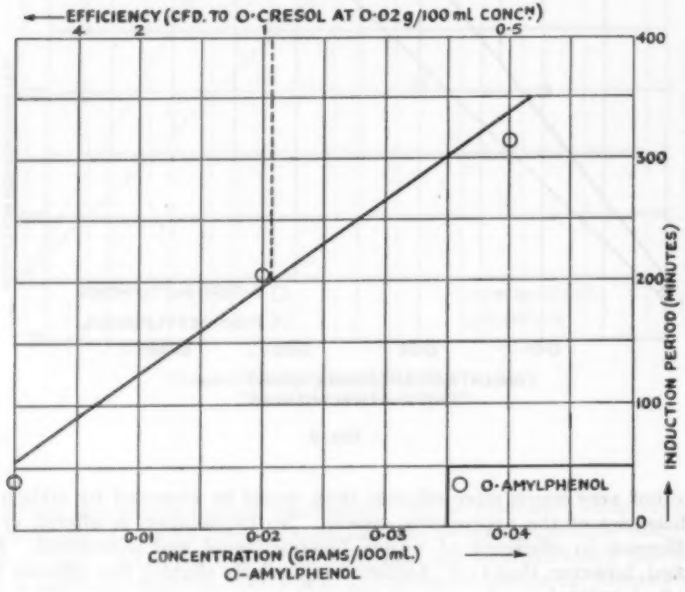
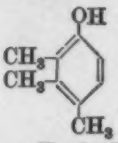


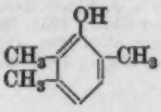
FIG. 7.

the results for one concentration only, however. The third case where this effect might have been noted is in the case of *unsym.*-hemimellitenol and

1 : 2 : 5-trimethyl-6-hydroxybenzene, but, owing to lack of time, it was not possible to synthesize the latter phenol.



unsym.-Hemimellitenol.



1 : 2 : 5-Trimethyl-6-hydroxybenzene.

It would be interesting to see if the critical oxidation potentials [12] of the above three pairs of phenols show any discrepancy due to an *ortho* effect, or if this effect is noticeable in the relative strengths of the phenols as reflected by rates of esterification, etc. The critical oxidation potential of 1 : 2 : 6-xylenol is cited by Egloff *et al.*, in a comparison of this property with inhibitor efficiency,[13] as equal to that of 1 : 2 : 4-xylenol, but in the case of the former phenol the potential is a calculated one, and obviously assumes the equality of *ortho*- and *para*-methyl substitution irrespective of the possibility of an *ortho* effect.

Mesitol is another example of a phenol possessing two *ortho* substituents, and its efficiency is not as great as might be expected from the fact that it contains two *ortho*- and one *para*-methyl groups. In fact, it is not as efficient as ψ-cumenol, which contains only one *ortho*-, one *para*-, and one *meta*-methyl group.

The type of alkyl substituent in the *para* position does not appear to alter the molecular efficiency, since the molecular efficiencies of *p-tert.*-butylphenol and *p-iso*-octylphenol are equal to that of *p*-cresol. From the limited results obtained on *o*-amylphenol, however, it does appear, in agreement with Egloff's observations on thymol and carvacrol (Table I above), that molecular efficiency is affected by the type of *ortho* alkyl substituent.

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